

High Resolution Vacuum Ultraviolet Pulsed Field Ionization Photoelectron Band for $\text{OCS}^+(\text{X}^2\Pi)$: An Experimental and Theoretical Study

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INTRODUCTION

The vacuum ultraviolet pulsed field ionization photoelectron (PFI-PE) band for $\text{OCS}^+(\text{X}^2\Pi)$ in the energy region of 11.09-11.87 eV has been measured using high-resolution monochromatic synchrotron radiation. The ionization energies (IEs) for the formation of the (0,0,0) $\text{X}^2\Pi_{3/2}$ and (0,0,0) $\text{X}^2\Pi_{1/2}$ states of OCS^+ are determined to be 11.1831 ± 0.0005 eV and 11.2286 ± 0.0005 eV, respectively, yielding a value of 367 ± 1.2 cm^{-1} for the spin-orbit splitting. Using the internally contracted multi-reference configuration interaction approach, three-dimensional potential energy functions (PEFs) for the $\text{OCS}^+(\text{X}^2\Pi)$ state have been generated and used in the variational Renner-Teller calculations of the vibronic states. The energies of all vibronic states ($J=P$) for $J = 1/2, 3/2, 5/2$, and $7/2$ have been computed in the energy range of ≈ 4000 cm^{-1} above the IE [$\text{OCS}^+(\text{X}^2\Pi_{3/2})$] for the assignment of the experimental spectrum. By a minor modification of the *ab initio* PEFs, good correlation is found between the experimental and theoretical Renner-Teller structures. Similar to the PFI-PE bands for $\text{CO}_2^+(\text{X}^2\Pi_g)$ and $\text{CS}_2^+(\text{X}^2\Pi_g)$, weak transitions have been detected in the PFI-PE band for $\text{OCS}^+(\text{X}^2\Pi)$, which are forbidden in the Franck-Condon approximation. The non-vanishing single-photon ionization cross sections involving the excitation of the bending vibrational modes of OCS^+ , CO_2^+ , and CS_2^+ in their ground electronic states are attributed to the symmetries of the geometry dependent electronic transition dipole operator components.

EXPERIMENT

The design and combined performance of the high-resolution monochromatic VUV synchrotron source and the photoion-photoelectron apparatus has been described previously.¹⁻⁵ The high resolution VUV synchrotron source essentially consists of an undulator with a 10 cm period (U10), a gas harmonic filter, and a 6.65m off-plane Eagle mounted monochromator. The photon energy corresponding to the U10 undulator fundamental peak can be tuned easily to cover the energy range of 8-25 eV. Using Ne (pressure ≈ 30 Torr) as the filter gas in the present experiment, VUV radiation due to higher undulator harmonics with photon energy above the ionization energy (IE) of Ne (21.56 eV) was greatly suppressed (suppression factor = 10^{-4}) before entering the monochromator. Thus, the present experiment was essentially free from interference by photoionization and photoexcitation effects caused by higher order undulator radiation. The grating employed was an Os coated 4800 l/mm grating (Hyperfine Inc.) with a dispersion of 0.32 Å/mm. The monochromator entrance/exit slits used vary in the range of 75-400 μm , which correspond to wavelength resolutions of 0.024-0.128 Å (FWHM).

A continuous molecular beam of pure OCS was produced by supersonic expansion from a room temperature nozzle (diameter = 0.127 mm) at a stagnation pressure of ≈ 760 Torr. The molecular beam was skimmed by a home made conical skimmer (diameter = 1 mm) before intersecting the

Figures 1a (top) and 1b (bottom). OCS^+ ($X^2\Pi$), Rotational Temperature $\sim 100\text{K}$

rotational branches in the photoionization transition. The rotational profiles appear to shade toward the red, consistent with the fact that the C-S bond distance in $\text{OCS}^+(\text{X}^2\Pi)$ is longer than that in $\text{OCS}(\text{X}^1\Sigma^+)$.

For a linear molecule, such as $\text{OCS}^+(\text{X}^2\Pi)$, with v_2^+ bending quanta, the vibrational angular momenta along the molecular axis can have values $l_v\hbar$, where $l_v = v_2^+, v_2^+-2, 1$, or 0. Since the electronic orbital angular momentum has a nonzero projection of Λ_h along the molecular axis, the Renner-Teller coupling between Λ and l_v forms a new quantum number, $K = |\Lambda \pm l_v|$. Including

coupling of the projection of the spin angular momentum on the molecular axis (Σ), the projected angular momentum is $P = \Lambda + l_v + \Sigma$. In Table III, the calculated vibronic levels for the electronic ground state of OCS^+ are given for energies up to $\approx 4000 \text{ cm}^{-1}$ above the $(0,0,0)$ $\text{X}^2\Pi_{3/2}$ ground state. In the present work, we have performed calculations for $J = 1/2, 3/2, 5/2$, and $7/2$, i.e., K could take values 0, 1, 2, and 3 (Σ, Π, Δ , and Φ vibronic states), and only the $J=P$ levels (each having its own rotational stack) are given. The μ levels can be approximately associated with the lower potential component (A') and the κ levels with the higher one (A''). The energies [$\Delta v(\text{theo})$ in cm^{-1}] in Table III for the vibronic levels, $(v_1^+, v_2^+, v_3^+) ^2\Sigma_{1/2}^+ (^2\Sigma_{1/2}^-, ^2\Pi_{3/2,1/2}, ^2\Delta_{5/2,5/2}, \text{ and } ^2\Phi_{5/2,7/2})$, of the $\text{OCS}^+(\text{X}^2\Pi)$ state are given with respect to the energy of the $(0,0,0)$ $^2\Pi_{3/2}$ level.

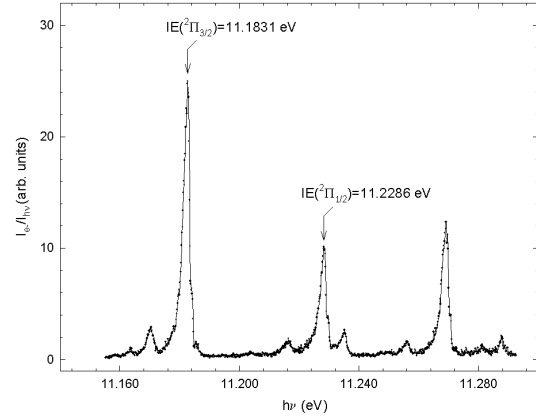


Figure 2. $\text{OCS}^+(\text{X}^2\Pi)$, Rotational Temperature $\sim 50 \text{ K}$

Due to the Renner-Teller coupling and the strong anharmonic resonances, the assignments of the calculated vibronic levels of $\text{OCS}^+(\text{X}^2\Pi)$ to (v_1^+, v_2^+, v_3^+) harmonic vibrational states are not straightforward except for the levels lying within $\approx 1700 \text{ cm}^{-1}$ above the $(0,0,0)$ $\text{X}^2\Pi_{3/2}$ state of OCS^+ . The harmonic vibrational quantum numbers were attributed to particular states by inspection of the contour plots for both vibrational parts and the weights of the basis functions in the vibronic wavefunctions. In the $^2\Sigma$ states, we could assign all levels to Fermi polyads, even though in some cases the $^2\Sigma^+$ members of a polyad were found to interact with different $^2\Sigma^-$ members of another polyad. The same situation is found in the $^2\Pi$ and $^2\Delta$ states, where in some cases strong interactions between different polyads in the μ and κ states exist. In the $^2\Phi_{5/2}$ states the distinction between the μ and κ states is hardly possible and, therefore, has not been included in the assignment of the PFI-PE peaks of the OCS spectrum shown in Figs. 1(a) and 1(b). We find also in many cases K-coupling (i.e., the $^2\Pi$ states mix with the $^2\Delta$ states etc.). A reliable analysis of this effect requires more accurate PEFs than those of the present work. Referring to Table III, the levels with the corresponding unique level designations are marked by asterisks. A, b, c, etc designate Fermi polyad members. The numerical value, such as 05, designates $v_3^+ = 0$, and $2v_1^+ + v_2^+ = 5$ (i.e., polyad five) etc. The prime in, e.g., 07' designates the upper Renner-Teller polyad. The equal sign means that the level belongs to two polyads. Generally, for all higher energy levels the assignments with harmonic quantum numbers are only tentative.

CONCLUSIONS

We have obtained a high resolution PFI-PE spectrum for OCS in the energy range of 11.09-11.87 eV. In addition to strong photoelectron bands assignable to $(v_1^+, 0, v_3^+) {}^2\Pi_{3/2}$ and $(v_1^+, 0, v_3^+) {}^2\Pi_{1/2}$ for $\text{OCS}^+(\text{X}^2\Pi)$, weaker Renner-Teller structures are observed for the first time. Accurate theoretical predictions for the Renner-Teller levels for the $\text{OCS}^+(\text{X}^2\Pi)$ state have also been obtained. The observed transitions in the PFI-PE spectrum are assigned satisfactorily by using the calculated energy positions of the vibronic levels.

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